Martensitics

stainless steel flat product | Acerinox Europa

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ACERINOX

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Martensíticos

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Introduction

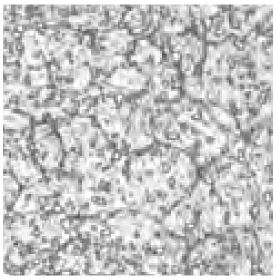
Stainless steels are ferrous alloys with a minimum content of 10.5% Cr in their composition and up to 1.2% C.

Under these premises there are a large number of alloys that are sorted into five groups or families.

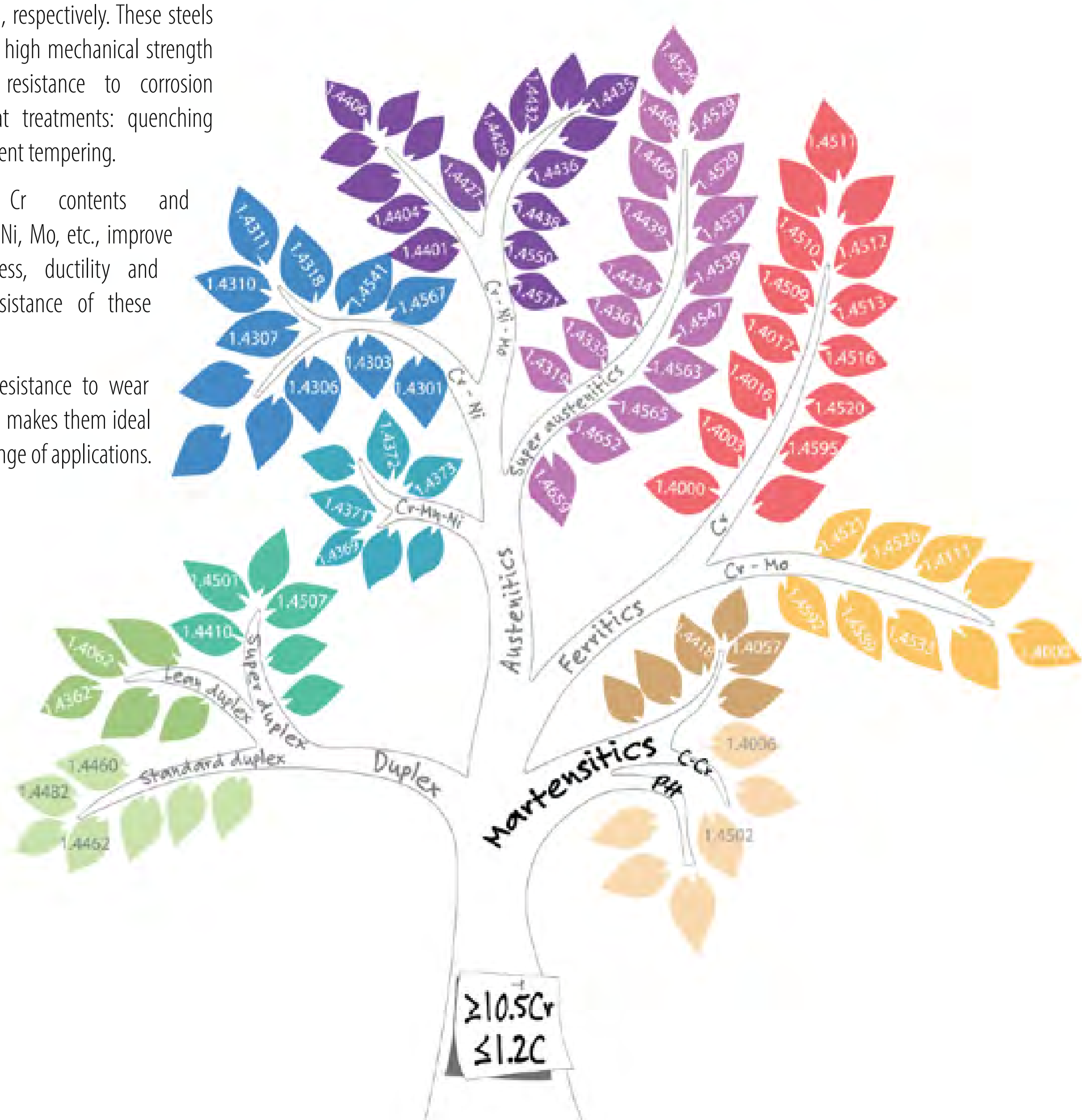
Martensitic stainless steels are iron alloys basically containing carbon and chromium in the range of 0.10-0.60% and 12-14%, respectively. These steels acquire their high mechanical strength and good resistance to corrosion through heat treatments: quenching and subsequent tempering.

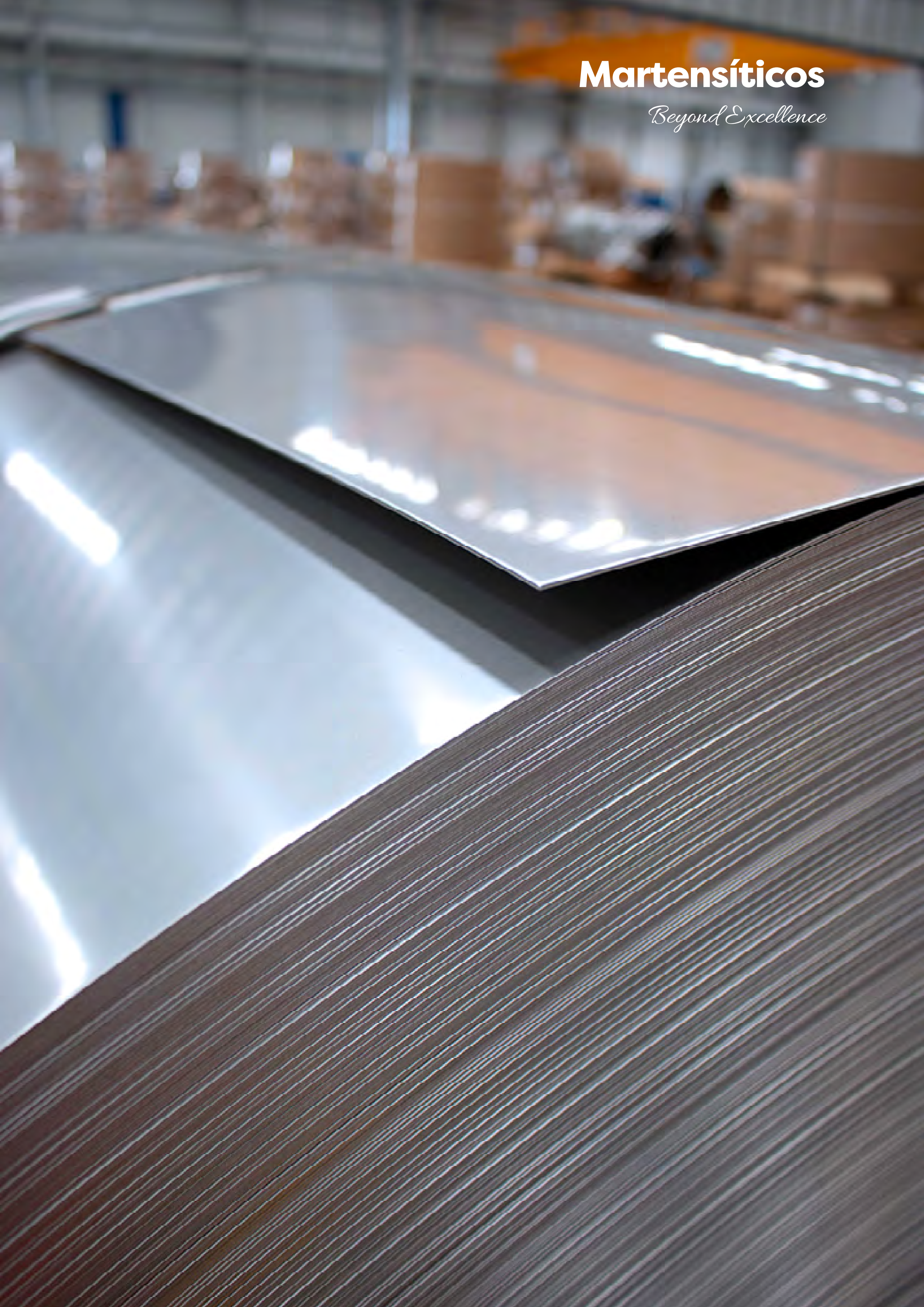
Increasing Cr contents and additions of Ni, Mo, etc., improve the toughness, ductility and corrosion resistance of these grades.

Their high resistance to wear and abrasion makes them ideal for a wide range of applications.



In their service condition, most martensitic stainless steels have a microstructure consisting of martensite and dispersed carbides.

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History

In 1912, Harry Brearley searched on the problem of erosion and contamination of rifle barrels at the Royal Arms Factory in Enfield. He had already worked with 5-6% Cr steels and found that alloys with a higher content of this element could be a solution to the problem of weapons, due to their high melting point.

On August 20, 1913, Brearley first melted steel with a content of 12.8% chromium, 0.24% carbon, 0.22% manganese, and 0.2% silicon. This was the first commercial stainless steel casting. Although this steel did not meet the expectations for the manufacturing of barrels, Brearley observed that reagents that normally attack the steel did not affect that new alloy or did it very slowly. In addition, depending on the heat treatment, the behaviour of the metal was different, so he proposed the use of this alloy for other applications, including cutlery. This alloy is known today as **martensitic** stainless steel.

By the time, Sheffield had became the centre of the knife industry in England for 300 years. The idea of a "rust free" steel did not convince the main manufacturers. However, two of them, Ibberson and Dixon, ran tests on Brearley's first casting material and found that it was impossible to forge, difficult to harden and dirty. It was in June 1914 when Brearley met Ernest Stuart, manager of Robert F. Mosley company, who became interested in this steel that did not corrode. After some failed tests due to the material being too hard and brittle, Stuart invited Brearley to witness his knife production, making his expertise in forging and tempering treatments essential for the successful make of the early martensitic stainless steel knives. In October 1914, Harry Brearley stated that this material seemed especially appropriate for the manufacture of shafts, pistons, pumps, fans, valves, and knives.

In this same period in Germany, Maurer and Strauss and in America, Haynes, Armstrong, Becket and Dantsized, experimented with steel alloys with high chromium content for possible commercialization.

1909 Guillet, France, publishes the results of his studies on Fe-Cr and Fe-Ni and classifies them according their structure (martensitic, ferritic and austenitic).

1913 Harry Brearley discovers martensitic stainless steel, former 420 and produces the first commercial cast.

1914 Production of 50 tonnes of cutlery stainless steel by Thomas Firth & Sons, Sheffield.

1914 - 1918: I World War

Firth increases by 14% chromium and delivers all the production for aircraft engine exhaust valves (Firth's Aeroplane Steel: FAS).

1915 Firth-Sterling, Firth & Sons American subsidiary, produces martensitic steel similar to today's 420. Brearley's Canadian patent.

1916 USA patent. Brearley. Similar grade to today's 420. Cr: 9 - 16%; C: 0.7% max.

1917 Carpenter (USA): first martensitic steel for Liberty plane and cutlery.

1920 Latrobe, USA, developes the first mirror-finish cutlery steel. 1st Carpenter patent. Similar to 422.

1928 Carpenter introduces the world's first free-machining stainless steel (today's 416).

1930 1940 In this decade, new manufacturing processes facilitate under 0.1% low carbon.

1962 Carpeter's *Project 70* : 416 improved machinability.

1968 Crucible registers grades 416 and 416 Plus X patents.

1996 Armco Steel produces 410 Cb. Nb addition as stabilizer that improves its corrosion resistance at hign temperature. Higher fluence resistance.

Graphite electrodes in the arc electrical furnaces enable reaching temperatures quite above the steels' melting temperatures. At the end of this process stage, the optimal composition ready for the final refinement at the AOD converter is achieved.

What makes them different?

The hardening or quenching treatment comprises a first stage, called the austenitization, in which the material's temperature is raised until a mostly austenitic microstructure is achieved, and then a cooling stage in which austenite transforms into the target martensite. This constituent or phase is highly resistant and hard, but also brittle, and must be softened through subsequent tempering treatment.

Depending on the particular conditions of the above processes, a balance of properties of hardness, wear resistance, corrosion resistance, etc. can be obtained for the end use concerned.

Their outstanding level of hardness, primarily derived from the carbon content, is maintained at high temperatures, even up to 650ºC in those types alloyed with V, Nb, Co, etc.

Martensitic stainless steels have thermal and electrical conductivity values closer to those of carbon steel than austenitic, ferritic, and duplex stainless grades, which can be an advantage in certain applications.

They provide a particularly favourable solution in terms of cost for not being alloyed with significant levels of nickel, and for the same reason they have greater price stability.

Compared to aluminium, martensitics have important advantages, including structural ones thanks to their greater mechanical resistance and better weldability due to more favourable properties in terms of thermal expansion, thermal conductivity and electrical conductivity.

Both in the supply condition and after the heat treatments applied to obtain the final aim properties, they are steels featuring a ferromagnetic micro structure.

These steels can suitably be welded by the usual methods of electrical arc, electrical resistance, etc., although certain measures must be taken to control the heating and cooling stages in order to avoid cracking issues.

Once the metallurgical process has finished, the material is delivered to the cutting lines to adapt its size to our customers' needs.

Grades. Equivalences

As a result of innovation and development, in Acerinox we present the following grades of martensitcs, which adapt to the situations that may arise.

ACERINOX	EURONORM		ASTM	UNS
ACX 360	EN 1.4028	X30Cr13	420	S42000
ACX 370	EN 1.4034	X46Cr13	420	S42000
ACX 380	EN 1.4116	X50CrMoV15	420MoV	--
ACX 390	EN 1.4031	X39Cr13	420	S42000
ACX 430	EN 1.4021	X20Cr13	420	S42000

Chemical composition

	C	Si	Mn	P	S	Cr	Mo	V
ACX 360	0.26-0.35	≤1.00	≤1.50	≤0.040	≤0.015	13.00-14.00		
ACX 370	0.43-0.50	≤1.00	≤1.00	≤0.040	≤0.015	13.00-14.50		
ACX 380	0.45-0.55	≤1.00	≤1.00	≤0.040	≤0.015	14.00-15.00	0.50-0.80	0.10-0.20
ACX 390	0.36-0.42	≤1.00	≤1.00	≤0.040	≤0.015	13.00-14.50		
ACX 430	0.16-0.25	≤1.00	≤1.00	≤0.040	≤0.015	12.00-14.00		

Product. Size. Finish

HOT ROLLED

	THICKNESS (mm)	WIDTH (mm)	LENGTH (mm)
COIL	3.0 - 6.8	≤1250	-
SHEET	3.0 - 6.8	600 - 1250	≤9300

COLD ROLLED

	FINISH	THICKNESS (mm)	WIDTH (mm)	LENGTH (mm)
COIL	2D / 2B / 2G	0.8 - 3.0	≤1250	-
SHEET	2D / 2B / 2G	0.8 - 3.0	150 - 800 (thickness 0.8-1.2)	300 - 3100
			800 - 1250 (thickness >1.2)	300 - 6000

Specifications & tolerances

Acerinox Europa supplies martensitic stainless steels according to the following specifications:

EN 10088-2	ASTM A240

Mechanical properties

Martensitic stainless steels have A_1 and A_3 transformation points, what enables being hardened by thermal treatment. It consists of quenching to make the necessary martensitic structure and further tempering for the stress relieving of this phase.

The mechanical properties of these steels in annealed condition (supply), featuring a microstructure of ferrite and carbides, are shown in adjacent table.

According to EN 10088-2	**Tensile strength Rm (MPa, N/mm²)**	**Elongation (%)**	**Hardness HRB**
ACX 360	max. 740	min. 15	max. 97
ACX 370	max. 780	min. 12	max. 99
ACX 380	max. 850	min. 12	max. 100
ACX 390	max. 760	min. 12	max. 98
ACX 430	max. 700	min. 15	max. 95

Physical properties

		ACX 360	**ACX 370**	**ACX 380**	**ACX 390**	**ACX 430**
Density (kg/dm³)	20ºC	7.7				
Modulus of elasticity (GPa)	20ºC	215	215	215	215	215
	100ºC	212	212	212	212	212
	200ºC	205	205	205	205	205
	300ºC	200	200	200	200	200
	400ºC	190	190	190	190	190
Specific heat (J/kg K)	20ºC	460				
Thermal conductivity (W/m·K)	20ºC	30	30	30	30	30
Electrical resistivity (Ω·mm²/m)	20ºC	0.65				
Mean coefficient of linear expansion between 20ºC and (10^{-6}x K^{-1})	100ºC	10.5	10.5	10.5	10.5	10.5
	200ºC	11.0	11.0	11.0	11.0	11.0
	300ºC	11.5	11.5	11.0	11.5	11.5
	400ºC	12.0	12.0	11.5	12.0	12.0

Fabrication

THERMAL TREATMENTS

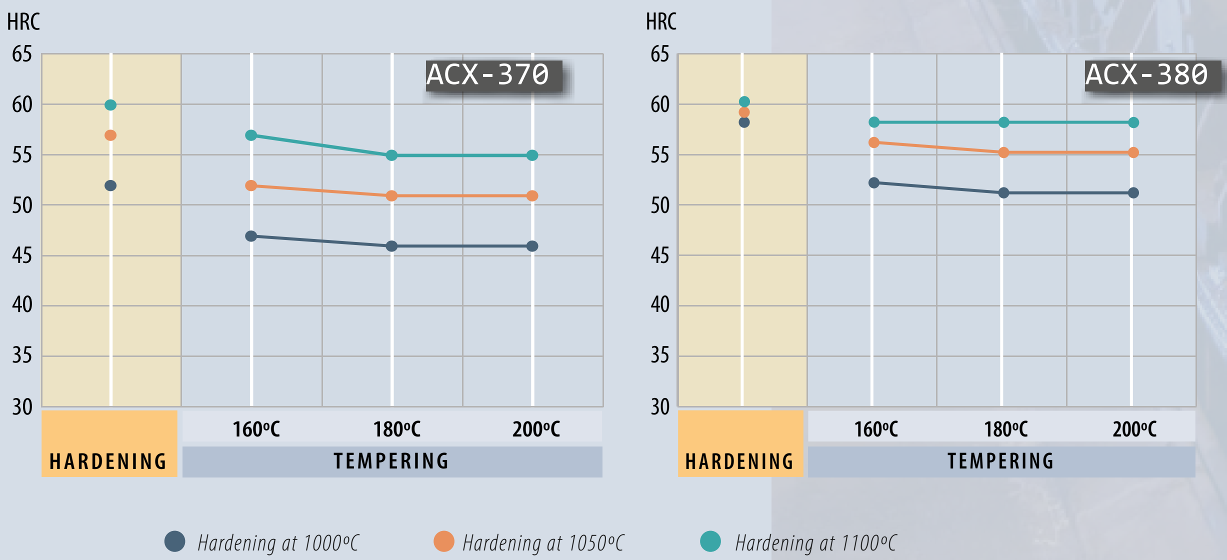
Hardening

This process is carried out in two steps: heating to a temperature above A_3 (austenitization) in order to achieve a mostly austenitic microstructure which is subsequently transformed upon cooling into martensite, a phase of high hardness and brittleness.

Due to the alloy grade of martensitic stainless steels, this transformation can be achieved by air cooling. Austenitization is not recommended at temperatures significantly above 1050ºC to avoid the risk of retained austenite after cooling.

Tempering

This heat treatment is carried out on the previously hardened steel in order to reduce its high brittleness and optimize its mechanical properties (toughness, hardness, etc.) and corrosion resistance. The recommended temperature range for tempering is 180-220ºC.



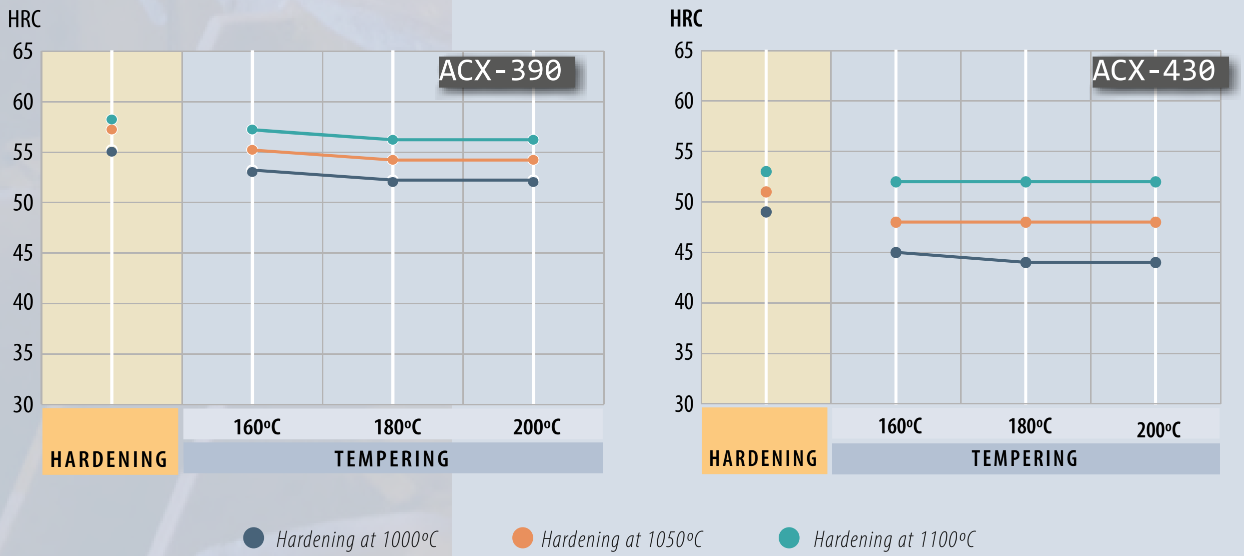
HARDENABILITY CURVES

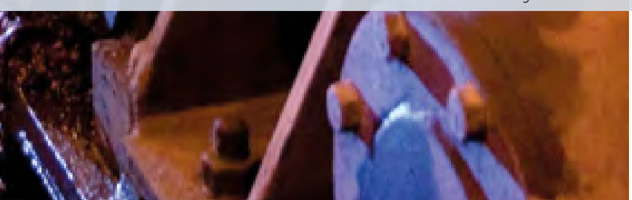
Treatments conditions:

Hardening: 10 minutes + air cooling
Tempering: 1 hour + air cooling

While shearing the excellent group of mechanical and corrosion resistance properties of martensitic stainless steels, the ACX range of martensitics also permits to choose the most appropriate grade for the specific application we are working with and the available manufacturing process.

Therefore, for example, it is possible to choose between the relatively moderate hardness of ACX 430 and higher ones that are possible from the carbon contents between 0.35 and 0.55%. In these cases, with the additional option to select a quite improved corrosion resistance (ACX 380).





WELDING

In any structural condition, martensitic stainless steels can be conveniently joined using most of the welding methods of electric arc, resistance, high-power beams, etc. However, in addition to the usual requirements necessary for welding stainless steel, such as cleaning the work area, edge preparation, removing moisture from consumables, etc., in the case of martensitic steels special precautions must be taken due to their high hardenability. In this sense, the sensitivity of these steels increases with the carbon content, and it is recommended to consider the following preventive measures to control the risk of embrittlement due to the inherent stresses in the process and contamination of various kinds:

- Use of preheating (200-300ºC) and postheating (650-750ºC), to reduce the temperature variations involved in the process and temper the reformed martensite, respectively.
- Use rather high thermal inputs to avoid too high cooling rates.
- Autogenous welding (without filler material) of these steels is possible. When filler material is used, it must be of similar composition or overalloyed (austenitic/duplex) in respect to the base material.
- In shielding gases the presence of hydrogen and nitrogen must be completely avoided.
- Pickling: for the first stage of the finishing process of weld affected surfaces, including the bead itself and the adjacent oxidized areas, there are different mechanical (brushing, grinding, shot blasting) and chemical (pastes, acids, electrochemical cleaning) methods. The choice of one or the other solution will depend on the practical, safety, etc. constraints in the relevant case.
- After the removal of oxidation products by pickling, the natural protective layer of stainless steel can be restored spontaneously in air, although this process is not immediate. If for any reason it is necessary to speed it up, you have to employ nitric acid then follow with a water rinse.

When welding procedures will not be feasible, or for dissimilar joints, martensitic stainless steels could be joined by either soldering, brazing or braze welding which are processes involving lower thermal shock.

Dissimilar welding

In many applications welding steels with different compositions is necessary. For the welding of AISI 420 martensitic grade and other stainless steel, a filler material of types 309 or 410-420 is generally recommended. In the case of joining with a carbon steel, the use of filler with a composition compatible with this type of steel is recommended.

Specific conditions for the welding of martensitic stainless steels can be found in the publications "Welding and cutting of stainless steels" by Manuel Aracil, CEDINOX and "The welding of stainless steels" by Pierre-Jean Cunat, EURO INOX.

Welding and cutting of stainless steels

The welding of stainless steels

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Selecting the best welding conditions, filler metal and shielding gas for the specific welding process and application will ensure the production of joints with mechanical, physical and chemical properties equal or superior to those of the base metal.

Some recommendations

Transport & handling

Before shipping, make sure every chain and steel element is not in contact with stainless steel rebar. Raffia or wooden elements must be used at possible contact places.

Avoid carbon steel slings, use nylon or polypropylene ones wherever possible.

When outside storage is required, material should be covered by a waterproof canvas.

When stainless steel has to be moved with lift trucks, the forks should be protected with nylon.

Avoid contact with the ground using wooden blocks and store stainless steel and carbon steel separately. This way we avoid problems with contamination by oils, dirt or by contact among different materials.

Manufacturing & installation

Make sure stainless steel is contamination free before starting to work. If there is any, it will be removed by pickling or mechanical means (*).

Whether, for any reason, the surface is painted, you need to prime/prepare the surface by acid pickling or abrasion. Follow the instructions of the paint manufacturer.

If cleaning is required, do it with pressurized water. Do not use sea or brackish water.

(*) Contact your supplier

Temperature and time for austenitization should be 1050ºC and 10 minutes, following air cooling together with one hour tempering at 200ºC are general conditions to obtain good final properties.

Structure and properties of martensitic stainless steels are quite sensitive to hardening conditions. Those should be applied as homogeneously as possible in batch processes. In this sense, special attention should be paid to the stacking and disposition of the material into the furnace to avoid the "shadowing" effect among them.

The necessary finishing operations such as polishing, cutting, sharpening, etc, must be carried out avoiding over heating in localized areas of the piece. Temperatures higher than 400ºC can cause oxidation ("blueing") and impair the quality obtained through previous thermal treatments properly applied.

Surface maintenance

Regular cleaning is mandatory to keep unaltered surfaces indefinitely and obtain the best performance of stainless steel.

Chloride products must be avoided. In case of use, the contact must be minimum and must be followed by a thorough rinse with plenty of water..

For cleaning, it is recommended the use of water and neutral soap applied with a soft cloth or brush that do not scratch the surface. To finish, always rinse with plenty of water to remove any trace of the cleaner.

More information about stainless steel cleaning through this code.

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Sited in Campo de Gibraltar (Cádiz, Spain), Acerinox Europa has its own seaport in a privileged location which facilitates materials transit, including reception of raw materials and shipping finished products to destination.

Applications

	ACX 360	ACX 370	ACX 380	ACX 390	ACX 430
Cutting tools	✓	✓	✓	✓	✓
Cutlery	✓	✓	✓	✓	✓
Professional cutlery		✓	✓	✓	
Brake discs		✓		✓	✓
Automotive		✓			✓
Dental and surgical tools	✓	✓		✓	✓
Paper and petrochemical industry	✓	✓			✓
Manual tools		✓			✓
Fitting accessories					✓
Springs	✓				✓
Mechanical wear parts	✓	✓	✓	✓	✓
Printing industry	✓				
Textile machinery industry					✓
Flow control					✓

By thermal treatment, martensitic stainless steel can develop an excellent combination of mechanical resistance, hardness and wear resistance, whilst keeping a moderate corrosion resistance.

When supplied, these stainless steels show good performance in ordinary transformation operations such as stamping, cutting, punching, machining, bending, etc.

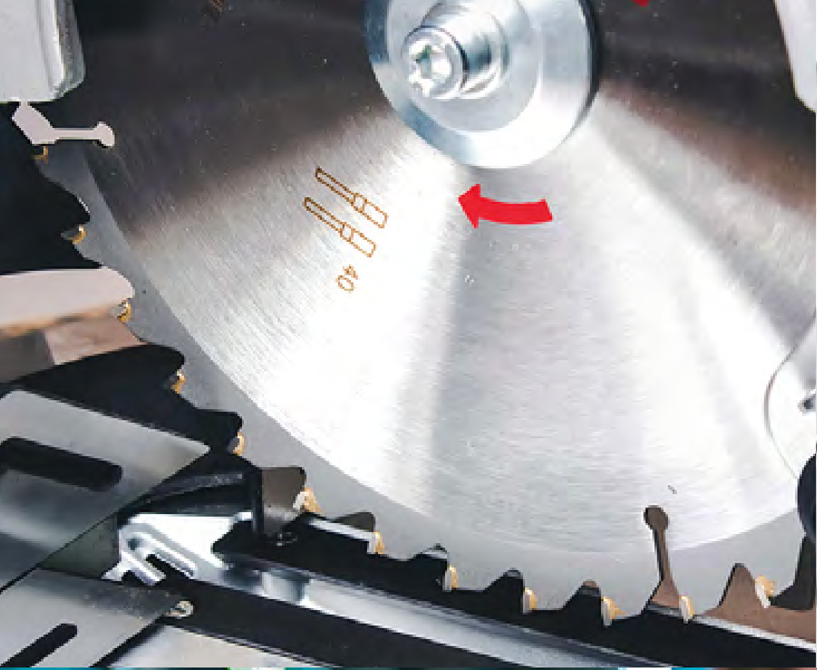
Both in delivery state or already heat treated, they can be welded following specific recommendations.

They also show good atmospheric corrosion resistance, as in drinking water and medium aggressive chemical environments, even in chloride presence if correct cleaning/ conditioning maintenance is applied after being used or having suffered a surface modification from oxidation or decarburization processes. In that regard, it is recommended to contact our Technical Department in order to get accurate information.

Compared to carbon steel, some of their physical properties are more similar than to those of austenitic or duplex steels. Therefore they mean an outstanding improvement in terms of corrosion resistance within a compatible cost context.

On the other hand, martensitic stainless steels can reach higher mechanical resistance than most stainless steels even if these have been cold worked or precipitation hardened.

These characteristics make them suitable not only to consolidated applications such as cutlery, surgical tools or mechanical elements but also for others where typical solutions show evident limitation in terms of performances, manufacturing feasibility, durability, maintenance, etc.



The martensitic stainless steels introduced in this catalogue provide optimal solution for numerous industrial and daily scenarios.

Certificates

Collaboration with organizations:

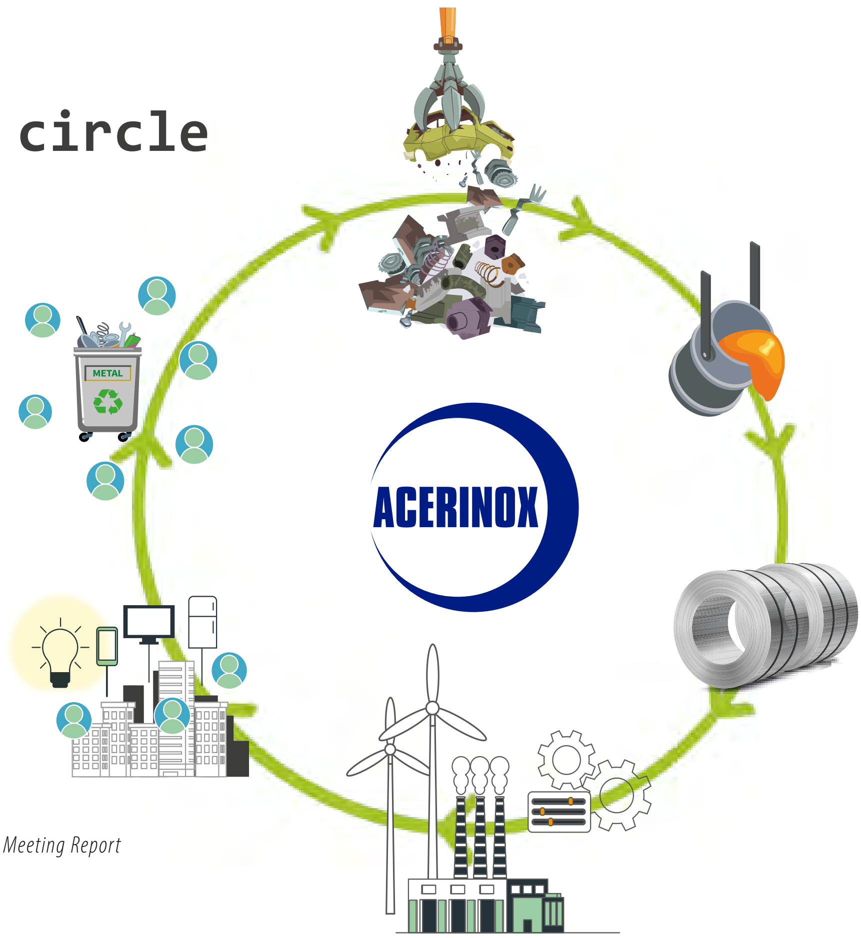
Complete information on Acerinox Europa certificates, here:

ESG ratings:

Sustainable circle

"Acerinox uses more than 90% recycled materials to produce stainless steels and high performance alloys that are durable and eternally recyclable without losing their characteristics. By recovering our waste, of which we already recycle more than 80%, we are without a doubt the paradigm of the circular economy.

*We efficiently manufacture stainless steels and high-performance alloys with a respectful approach and we are committed to a responsible management model that helps protect the planet, reduce inequalities, and promote a more prosperous and sustainable world."**



** Chief Executive Officer's. 2024 Annual General Meeting Report*

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In Acerinox Europa we have developed ECO ACX martensitics with 50% carbon footprint reduction compared to our standard martensitics. It means the lowest carbon footprint in the market within this family.

Acerinox: the confidence of a strong group

Acerinox Group is global leader in the manufacture of stainless steel and high performance alloys. We have factories with 3.5 million tonnes of melting shop capacity per year. Acerinox Europa, North American Stainless and Columbus Stainless manufacture flat product and Roldan, Inoxfil and North American Stainless (NAS) are long product producers. VDM Metals, worldwide leader in the fabrication and design of high performance alloys, is part of the Group from 2020. In November 2024, Acerinox completes the acquisition of Haynes International, U.S. leading manufacturer and marketer of technologically advanced high-performance alloys.

The factories and centres of Acerinox Group meet quality and environment controls according to the specific regulations of each country and to Environmental Management Systems. Our subsidiaries also exceed the requirements of the legislative demands in different areas such as quality, security or environment. We work in 79 countries to build a more sustainable society, meeting present and future needs thanks to our durable, hi-performance and respectful materials.

Acerinox Europa was the first integrated stainless steel factory in the world. Founded in 1970, the plant continues at the forefront as one of the most advanced factories in the sector thanks to a continuous investment policy.

With its own cargo seaport, Acerinox Europa is in a privileged location next to the straits that link the Atlantic with the Mediterranean.

With a melting shop capacity of one million tonnes, Acerinox Europa supplies mainly flat products to the European continent and material for producing long products to other plants within the Group.

TECHNICAL INFORMATION:

COMMERCIAL INFORMATION:

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NAS

INOXFIL

VDM Metals

COLUMBUS STAINLESS [Pty] Ltd

ROLDAN S.A.

HAYNES International

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